

ADSORPTION IMPEDANCE SPECTROSCOPY FOR A ROUGH ELECTRODE

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There has been increasing interest in understanding the electrode response for rough interface. Within the framework of the perturbation theory a theoretical model for adsorption impedance is proposed for the description of the diffusion-controlled adsorption step on a rough electrode.

The surface roughness of the electrode will cause a change in adsorption impedance diagram shape. It has been shown that the unequal accessibility of the interface in respect of diffusion leads to an increase in its capacity. At high frequencies, an increase in double layer capacity of rough electrodes is determined by the geometrical roughness factor. In the low-frequencies range, this capacity is affected by adsorption conditions. Extra capacity is determined by the peculiarities of the mass transfer of surface - active species to the rough electrode. On rough electrodes, the adsorbed species relaxation processes change due to change in the amount of adsorption as compared with plane electrodes, and their functional dependence on adsorption parameter changes either. In the Nyquist diagram, the appearance of the second loop is possible depending on the values of adsorption parameters and electrode roughness. The surface roughness causes a decrease in modulus of impedance.

It has been shown that adsorption of neutral molecules leads to phase angle constancy in the low - frequencies range for both plane and rough electrodes. The electrode roughness causes a change in phase angle and in the frequency range in which this constancy is observed.

For the case of weak roughness, we have derived a general expression for the roughness function. In complex plane, it is a distorted ellipse.

The effects that arise during adsorption from layer of finite thickness have been investigated. In this case, the ratio of diffusion layer thickness to roughness function is a characteristic parameter of the system. The finite thickness of diffusion layer gives rise to an additional relaxation time in the system.